CHAPTER FIVE

THERMOCHEMISTRY

5-1 Introduction

The preceding chapters have dealt with the physical properties and changes of state of pure substances or fixed mixtures of substances. We now consider the application of the first law of thermodynamics to chemical changes—a subject called thermochemistry. The subject is of great practical importance since it deals with the organization of the large amount of data concerning energies of chemical reactions. It also provides the foundation for obtaining chemical bond energies and hence for some aspects of theoretical chemistry.

This chapter also serves to introduce the general notation used in the application of thermodynamics to chemical change. The balanced equation for a chemical reaction is in the strict sense merely a particular affirmation that atoms are conserved. Thus the equation

\[ aA + bB + \cdots = mM + nN + \cdots, \]  

is no more than a statement that substances A, B, ..., if taken in the molar amounts \( a, b, \ldots \), will collectively contain the same number of each kind of atom as will substances M, N, ..., taken in the amounts \( m, n, \ldots \). The equation does not predict that the chemical change will in fact occur, or that if it does occur, that other types of reactions may not also be present. It is part of the practice of chemistry to devise experimental situations such that the measurements made can be analyzed into contributions from one (or more) specific chemical processes.

From the point of view of the first law, each substance has an internal energy and an enthalpy which are functions of the state of that substance. Thus \( E_A = f_A(V_A, T_A) \), \( E_B = f_B(V_B, T_B) \), and so on, and similarly \( H_A = f'_A(P_A, T_A) \), \( H_B = f'_B(P_B, T_B) \), and so on. To be complete, therefore, Eq. (5-1) should specify the state of each substance:

\[ aA(V_A \text{ or } P_A, T_A) + bB(V_B \text{ or } P_B, T_B) + \cdots = nN(V_N \text{ or } P_N, T_N) + mM(V_M \text{ or } P_M, T_M) + \cdots. \]  

(It is sufficient to give \( T \) and either \( P \) or \( V \) since the three are related by the equation of state for the substance.) The substances are not necessarily at the same temper-
ature and pressure or at the same temperature and molar volume. We then use the symbol \( \Delta \) as an operator which may be applied to any characteristic extensive property \( \mathcal{P} \) such as \( E, H, \) or \( V \) to signify the following operation:

\[
\Delta \mathcal{P} \quad \text{means} \quad (m\mathcal{P}_m + n\mathcal{P}_n + \cdots) - (a\mathcal{P}_a + b\mathcal{P}_b + \cdots)
\]  

(5-3)

or

\[
\Delta \mathcal{P} = \sum_{\text{products}} n_p \mathcal{P}_i - \sum_{\text{reactants}} n_r \mathcal{P}_i,
\]

where \( n_p \) and \( n_r \) are the stoichiometric coefficients in the balanced equation. The property \( \mathcal{P} \) is for the indicated substance in that state specified by the chemical equation. Thus the value of \( \Delta \mathcal{P} \) must always refer to a definite, completely described equation. In the case of reactions involving solutions chemical composition must be specified; the detailed thermochemistry of solutions is deferred until Chapter 9.

As an illustration, the reaction by which water is formed from hydrogen and oxygen might be written

\[
\text{H}_2 \ (\text{gas}, \ 25^\circ \text{C}, \ 1 \text{ atm}) + \frac{1}{2} \text{O}_2 \ (\text{gas}, \ 25^\circ \text{C}, \ 1 \text{ atm}) = \text{H}_2\text{O} \ (\text{liq}, \ 25^\circ \text{C}, \ 1 \text{ atm}).
\]

(5-4)

For this reaction \( \Delta H \) is

\[
\Delta H = H(\text{H}_2\text{O}) - H(\text{H}_2) - \frac{1}{2}H(\text{O}_2),
\]

(5-5)

where the individual enthalpies are per mole of the substance in the indicated state. Note that the phase (gas, liquid, solid) of the substance must be specified if there is any possible ambiguity.

Unlike the situation with some extensive quantities, such as volume or mass, we have no absolute values for the internal energy or enthalpy of a substance. Although the first law permits us to calculate changes in \( E \) or \( H \), its application never produces absolute values. The same is true in thermochemistry; \( \Delta E \) and \( \Delta H \) give the changes in internal energy and enthalpy that accompany a chemical reaction, and while either may be expressed in the form of Eq. (5-3), we do not know the separate \( E \) or \( H \) values. It is partly a consequence of this situation that much use is made of standard or reference states. Two systems of standard states are in use. The first is of convenience, 1 atm pressure and, if so specified, 25°C. In the case of a reaction for which the reactants and products are all in a standard state, such as Eq. (5-4), one writes \( \Delta E_{298}^0 \) or \( \Delta H_{298}^0 \), where the superscript zero means that the pressure is one atm and the subscript gives the temperature chosen. As will be seen, a large body of thermochemical data is reported on this basis.

The second system takes as the standard state the substance devoid of any thermal energy, that is, at 0 K. This is a more rational as well as a very useful approach and is developed in the Special Topics section. Its implementation does require either extensive knowledge of heat capacity data or sufficient spectroscopic information to allow evaluation of the various partition functions.

### 5-2 Measurement of Heats of Reaction: Relationship between \( \Delta E \) and \( \Delta H \)

The practice of thermochemistry involves the measurement of the heat absorbed or evolved when a chemical reaction occurs. That is, the determination is one of \( q \)
For simplicity, one attempts to choose conditions such that either volume is constant, so that no work is done, in which case \( \Delta E = q_v \), or such that pressure is constant, in which case \( \Delta H = q_p \). In either event, if heat is evolved, the reaction is said to be exothermic; \( q \) is negative and likewise the corresponding \( \Delta E \) or \( \Delta H \). If heat is absorbed, the reaction is said to be endothermic, and \( q \) and \( \Delta E \) or \( \Delta H \) are positive.

The equipment used to make such measurements is the calorimeter; it may be of either the constant-pressure or the constant-volume type. A simple illustration of the former is shown in Fig. 5-1(a). Insulation is provided by a Dewar flask and one observes the temperature change when the reactant dissolves in or reacts with the

\[
dE = \delta q - \delta w, \tag{5-6}
\]
\[
dH = \delta q + V \, dP. \tag{5-7}
\]
liquid or solution. Research calorimeters of this type are more elaborate, of course, and with the use of a thermistor or a thermocouple, temperature changes of as little as $10^{-5}^\circ{C}$ can be recorded. An electrical heating element allows the introduction of an accurately known amount of heat so that the heat capacity of the calorimeter can be determined. Since the calibration is electric, it is conventional to record calorimetric heats in joules rather than in calories.

The bomb calorimeter, illustrated in Fig. 5-1(b), is of the constant-volume type. Typically, a substance is ignited in oxygen by means of a spark and the temperature rise of the calorimeter is measured. The heat of reaction, corresponding in this case to a $\Delta E$, is again obtained through the known heat capacity of the calorimeter. These calorimeters are adiabatic; insulation confines the heat of reaction, which is given by the product of the temperature change and the heat capacity of the assembly. The temperature change should be small for several reasons. Heat losses through conduction and radiation are reduced and thus the error in correcting for them. One ultimately wishes to report the results as a standard enthalpy or energy change, such as a $\Delta H^\circ_{298}$ or a $\Delta E^\circ_{298}$, for a reaction in which reactants and products are at the same temperature and the necessary corrections may be troublesome and introduce error if much heating has occurred in the actual reaction.

Heat loss may be virtually eliminated by making the temperature difference between the calorimeter and its immediate surroundings essentially zero. The ice calorimeter used by Lavoisier and Laplace in 1780 [see Hoch and Johnston (1961)] is a classic example. Here, the reaction vessel, uninsulated, is packed in ice in a container having a drain spigot. The whole unit is packed in an outer layer of ice. The heat of reaction melts some of the inside layer of ice and is given by the amount of water collected from the drain. Since the inside and outside layer are both at $0^\circ{C}$, there is no net heat flow between them.

In a modern version, the reaction vessel is in thermal contact with a large heat reservoir, such as a block of metal, through a layer of thermoelectric semiconductor material. The temperature difference across the layer is given accurately by the potential difference and integration over the time of the experiment gives the total heat flow and hence the heat generated by the reaction. At no time, however, is there more than a very small temperature difference between the reaction vessel and the heat reservoir.

Calorimetry may also be used to measure light energy, the device being called a bolometer. The measurement is again one of temperature change, this time due to the energy delivered by the absorbed light. For example, one micromole of light quanta, or one microeinstein of light, at 500 nm wavelength corresponds to 0.2392 J. Pulsed lasers may deliver this much light in a single nanosecond pulse and here a ballistic calorimeter may be used. The light pulse is absorbed by a thermoelectric cavity and one sees a rapid increase in output voltage, followed by a decline as heat loss to the surroundings occurs. The instrument can be calibrated so that the maximum voltage gives the pulse energy.

To return to conventional calorimetry, the constant-volume type is generally used when a reactant or product is gaseous, as in combustion reactions. Since the measured heat is a $q_v$, one obtains a $\Delta E$ of reaction, and it is usually desirable to convert the result to a $\Delta H$ of reaction. It follows from the definition of $H$ that for a reaction

$$\Delta H = \Delta E + \Delta(PV),$$

(5-8)
and further

\[ \Delta H_{298}^0 = \Delta E_{298}^0 + P \Delta V, \quad P = 1 \text{ atm}, \tag{5-9} \]

where \( \Delta V \) is given by Eq. (5-3). Molar volumes of liquids and solids are not large and their contribution to the \( \Delta V \) of a reaction is usually of the order of a few cubic centimeters; the \( P \Delta V \) term of Eq. (5-9) would then amount to only about 1 cal. If gases are involved, however, the correction can be quite appreciable. If we let \( \Delta n_g \) denote the number of moles of gaseous products minus the moles of gaseous reactants, then the \( P \Delta V \) term becomes \((\Delta n_g)PV\). If the gases are nearly ideal, then an approximate form of Eq. (5-8) is

\[ \Delta H \approx \Delta E + (\Delta n_g)RT. \tag{5-10} \]

Thus in the case of Eq. (5-4)

\[ \Delta H_{298}^0 = \Delta E_{298}^0 - \frac{8}{3}(1.987)(298.1) = \Delta E_{298}^0 - 888 \text{ cal}. \]

The \( P \Delta V \) term for \( \text{H}_2\text{O}(l) \) amounts to only 18 cm\(^3\) atm or about 0.4 cal, so neglecting it introduces only a small error.

Constant-pressure calorimeters are especially convenient for reactions involving solutions. The process may be one of the dissolving of a substance in a solvent, in which case a heat of solution is obtained. Or a solution may be diluted by the addition of more solvent, so that a heat of dilution is obtained. Heats of chemical reactions may be studied by mixing two reacting solutions in the calorimeter. Since the calorimeter is open to the atmosphere or is at some constant pressure, the result gives \( \Delta H \) directly. Where high precision and accuracy are not required, the simple arrangement shown in Fig. 5-1(a) may be entirely adequate. If the heat of reaction is small, however, as for example is often the case with heats of dilution, the apparatus becomes much more sophisticated [see Barthel (1975)].

The principal chemical requirement in calorimetry is that the measured \( q \) must be assignable to a definite process. This means that the products must be well defined and preferably should result from a single, clean chemical reaction. Correction for incomplete reaction can be made, but it is very desirable that the reaction go to completion. In addition, the reaction should be fairly rapid; otherwise maintenance of the adiabatic condition of the calorimeter becomes very difficult. Most of the reactions of organic chemistry fail to meet one or another of these criteria, and for this reason organic thermochemistry deals mainly with combustion and hydrogenation; these processes generally can be made to go rapidly and cleanly. Heats of solution and dilution offer no great difficulty, and many inorganic reactions are easy to study. A good example of the latter would be a heat of neutralization of an acid by a base. On the other hand, coordination compounds often react too slowly for good calorimetry and are not easy to burn to well-defined products.

### 5-3 Some Enthalpies of Combustion, Hydrogenation, and Solution

The general type of calorimeter used for measuring heats of combustion was described in the preceding section. With excess pure oxygen present, most organic
compounds will burn cleanly to carbon dioxide and water. Halogens or nitrogen present in a compound may appear as a mixture of the element and its oxides, and the exact proportions of such products may have to be determined for each experiment. In working problems in this text, however, it will be sufficient for the reader to assume that only the free element is formed, that is, Cl₂, Br₂, I₂, or N₂.

Some typical enthalpies of combustion are collected in Table 5-1. They are generally quite large, and since it is the difference among various enthalpies of combustion that usually is wanted (see next section), a very high degree of precision is desirable. This has indeed been achieved; most of the results in the table are accurate to a few tens of calories or better. Notice that compounds containing oxygen, such as ethanol and acetic acid, have lower enthalpies of combustion than the corresponding hydrocarbons. In a sense such compounds are already partly "burned."

The hydrogenation of unsaturated hydrocarbons is another reaction that has been used. One procedure is to pass a mixture of hydrogen and the hydrocarbon

### Table 5-1. Some Enthalpies of Reaction

<table>
<thead>
<tr>
<th>Substance</th>
<th>Reaction</th>
<th>ΔHᶠᵉᵒˢᵗ</th>
<th>kcal</th>
<th>kJ</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Combustion</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂(g)</td>
<td>H₂ + 1/2O₂ = H₂O</td>
<td>-68.317</td>
<td>-285.84</td>
<td></td>
</tr>
<tr>
<td>C(graphite)</td>
<td>C + O₂ = CO₂</td>
<td>-94.052</td>
<td>-393.51</td>
<td></td>
</tr>
<tr>
<td>C(diamond)</td>
<td>C + O₂ = CO₂</td>
<td>-94.502</td>
<td>-395.40</td>
<td></td>
</tr>
<tr>
<td>CO(g)</td>
<td>CO + 1/2O₂ = CO₂</td>
<td>-67.636</td>
<td>-282.99</td>
<td></td>
</tr>
<tr>
<td>CH₄(g)</td>
<td>CH₄ + 2O₂ = CO₂ + 2H₂O</td>
<td>-212.86</td>
<td>-890.36</td>
<td></td>
</tr>
<tr>
<td>C₂H₆(g)</td>
<td>C₂H₆ + 3O₂ = 2CO₂ + 2H₂O</td>
<td>-310.62</td>
<td>-1299.63</td>
<td></td>
</tr>
<tr>
<td>C₂H₄(g)</td>
<td>C₂H₄ + 3O₂ = 2CO₂ + 2H₂O</td>
<td>-372.82</td>
<td>-1559.88</td>
<td></td>
</tr>
<tr>
<td>C₂H₂(g)</td>
<td>C₂H₂ + 2O₂ = 2CO + 4H₂O</td>
<td>-530.61</td>
<td>-2220.07</td>
<td></td>
</tr>
<tr>
<td>C₂H₆(l)</td>
<td>C₂H₆ + 3O₂ = 6CO₂ + 3H₂O</td>
<td>-789.08</td>
<td>-3301.51</td>
<td></td>
</tr>
<tr>
<td>C₂H₅OH(l)</td>
<td>C₂H₅OH + 3O₂ = 2CO₂ + 3H₂O</td>
<td>-326.71</td>
<td>-1366.95</td>
<td></td>
</tr>
<tr>
<td>CH₃COOH(l)</td>
<td>CH₃COOH + 2O₂ = 2CO₂ + 2H₂O</td>
<td>-208.5</td>
<td>-872.36</td>
<td></td>
</tr>
<tr>
<td><strong>Hydrogenation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₄(g)</td>
<td>C₂H₄ + H₂ = C₂H₆(g)</td>
<td>-32.747</td>
<td>-137.01</td>
<td></td>
</tr>
<tr>
<td>cis-CH₂CH=CHCH₃(g)</td>
<td>C₃H₆ + H₂ = C₄H₁₀(g)</td>
<td>-28.570</td>
<td>-119.54</td>
<td></td>
</tr>
<tr>
<td>trans-CH₂CH=CHCH₃(g)</td>
<td>C₃H₆ + H₂ = C₄H₁₀(g)</td>
<td>-27.621</td>
<td>-115.57</td>
<td></td>
</tr>
<tr>
<td><strong>Solution</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂SO₄(l)</td>
<td>H₂SO₄ + ∞H₂O = solution</td>
<td>-22.99</td>
<td>-96.19</td>
<td></td>
</tr>
<tr>
<td>H₂SO₃(l)</td>
<td>H₂SO₃ + 50H₂O = solution</td>
<td>-17.53</td>
<td>-73.34</td>
<td></td>
</tr>
<tr>
<td>HCl(g)</td>
<td>HCl + ∞H₂O = solution</td>
<td>-17.96</td>
<td>-75.14</td>
<td></td>
</tr>
<tr>
<td>NaOH(s)</td>
<td>NaOH + ∞H₂O = solution</td>
<td>-10.246</td>
<td>-42.87</td>
<td></td>
</tr>
<tr>
<td>NaCl(s)</td>
<td>NaCl + ∞H₂O = solution</td>
<td>0.930</td>
<td>3.89</td>
<td></td>
</tr>
<tr>
<td>Na₂C₂H₃O₂(s)</td>
<td>Na₂C₂H₃O₂ + ∞H₂O = solution</td>
<td>-4.3</td>
<td>-18.0</td>
<td></td>
</tr>
</tbody>
</table>

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b Combustion products are CO₂(g) and H₂O(l).

through an adiabatic calorimeter which contains some platinum catalyst. The rate of heating of the calorimeter is then determined for a known flow rate of the gases and, if necessary, the effluent gas is analyzed so that the degree of reaction may be found. As illustrated by the values in Table 5-1 enthalpies of hydrogenation are generally much smaller than those of combustion. It is now possible to obtain fairly accurate differences in enthalpies of hydrogenation of isomeric compounds.

The third type of experimental heat of reaction which is listed in the table is that of solution. These are known as integral enthalpies of solution (see Section 9-ST-1) and the reaction consists in mixing the pure substance with the indicated amount of water so that a solution is formed. Notice that a heat of solution may be large, as in the case of sulfuric acid, or small, as with sodium acetate. It may be positive, as with sodium chloride. Generally when heat is absorbed on dissolving, the value is small in magnitude. The heat of solution also depends on the final concentration obtained. As might be expected, the value (disregarding sign) tends to be larger for the limiting case in which an infinitely dilute solution is formed than for that involving some higher concentration. This last point is illustrated by the data for sulfuric acid and further in Table 5-3.

### 5-4 Combining \( \Delta H \) or \( \Delta E \) Quantities

Table 5-1 provides a very small sample of the many individual reactions and types of reactions that have been studied experimentally. A complete tabulation of such individual results would be both clumsy and difficult to use. The first step toward systematization, taken in Table 5-1, is to reduce all values to a standard pressure and temperature, the latter usually being 25°C (see the next section for the manner of doing this). The second and very important step is to report results as standard heats of formation (also discussed in the next section). The basis for doing this is that, according to the first law, \( E \) and \( H \) are state functions, so that \( \Delta E \) and \( \Delta H \) for a given overall process are independent of the path taken. The principle was formulated independently by Hess in about 1840 and is sometimes known as Hess’s law of constant heat summation.

The principle may be illustrated as follows. Consider the following two reactions:

1. \( \text{C}_2\text{H}_6(g) + \frac{1}{2}\text{O}_2(g) = \text{CH}_3\text{COOH}(l) + \text{H}_2\text{O}(l), \quad \Delta H^0_{298} = -164.5 \text{ kcal} \) \hspace{1cm} (5-11)
2. \( \text{CH}_3\text{COOH}(l) + 2\text{O}_2(g) = 2\text{CO}_2(g) + 2\text{H}_2\text{O}(l), \quad \Delta H^0_{298} = -208.3 \text{ kcal} \) \hspace{1cm} (5-12)

These correspond to first oxidization of ethane to acetic acid and then burning of the acetic acid to carbon dioxide and water. The net result of the two steps is simply the combustion of ethane:

\[ \text{C}_2\text{H}_6(g) + 3\frac{1}{2}\text{O}_2(g) = 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l), \quad \Delta H^0_{298} = -372.8 \text{ kcal} \] \hspace{1cm} (5-13)

It is a common procedure in chemistry to obtain the net result of a series of chemical steps by the algebraic summation of the corresponding equations. Thus Eq. (5-13) results from the addition of Eqs. (5-11) and (5-12) and the cancellation of \( \text{CH}_3\text{COOH}(l) \) since it appears once on each side of the equality sign. This procedure is always possible with balanced chemical equations, and the result must also be a balanced equation. The further conclusion of importance here is that the \( \Delta H^0_{298} \) quantities combine similarly. If we write each according to its detailed
meaning as given by Eq. (5-3) we have

\[
\Delta H_{298}^0 [\text{Eq. (5-11)}] + \Delta H_{298}^0 [\text{Eq. (5-12)}] = [H_{\text{CH}_3\text{COOH}} + H_{\text{H}_2\text{O}} - H_{\text{C}_2\text{H}_6} - \frac{1}{2} H_{\text{O}_2}] \\
+ 2 H_{\text{CO}_2} + 2 H_{\text{H}_2\text{O}} - H_{\text{CH}_3\text{COOH}} - 2 H_{\text{O}_2} \\
= [2 H_{\text{CO}_2} + 3 H_{\text{H}_2\text{O}} - H_{\text{C}_2\text{H}_6} - \frac{3}{2} H_{\text{O}_2}] .
\]

The quantities \( H_{\text{CH}_3\text{COOH}} \) cancel since each is for the same substance in the same state, and the result is just \( \Delta H_{298}^0 \) for the net equation (5-13). The sum of \(-164.5 \text{ kcal} \) and \(-208.3 \text{ kcal} \) is indeed \(-372.8 \text{ kcal} \).

The general conclusion is that \( \Delta H \) (or \( \Delta E \)) quantities add (or subtract) as do the corresponding equations provided that the substances that are cancelled are in the same state. This last requirement will necessarily be met if standard \( \Delta H \)'s are used.

The lack of dependence of \( \Delta H \) and \( \Delta E \) on path is useful in the following ways. It allows the calculation of a \( \Delta H \) or \( \Delta E \) for a process that is difficult or impossible to carry out directly or which simply has not yet been measured. As an example, one can determine experimentally the heats of combustion of graphite and of diamond:

\[
\text{C(graphite)} + \text{O}_2(g) = \text{CO}_2(g), \quad \Delta H_{298}^0 = -94.052 \text{ kcal}, \quad (5-14)
\]

\[
\text{C(diamond)} + \text{O}_2(g) = \text{CO}_2(g), \quad \Delta H_{298}^0 = -94.502 \text{ kcal}. \quad (5-15)
\]

We may subtract Eq. (5-15) from Eq. (5-14) to get

\[
\text{C(graphite)} = \text{C(diamond)}, \quad \Delta H_{298}^0 = (-94.052) - (-94.502) = 450 \text{ cal}. \quad (5-16)
\]

The conversion of graphite to diamond (or vice versa) is not a feasible laboratory reaction, but by combining the two enthalpies of combustion one obtains the desired \( \Delta H_{298}^0 \).

Enthalpies of combustion may, in fact, be used quite generally to obtain enthalpies of other reactions. Thus the reaction

\[
\text{C}_2\text{H}_4(g) + \text{H}_2(g) = \text{C}_2\text{H}_6(g)
\]

may be written as

\[
\text{C}_2\text{H}_4(g) + 3\text{O}_2(g) = 2\text{CO}_2(g) + 2\text{H}_2\text{O}(l), \quad \Delta H_{298}^0 = -337.23 \text{ kcal}, \quad (5-18)
\]

\[
H_2(g) + \frac{1}{2} \text{O}_2(g) = \text{H}_2\text{O}(l), \quad \Delta H_{298}^0 = -68.317 \text{ kcal}, \quad (5-19)
\]

minus

\[
\text{C}_2\text{H}_4(g) + \frac{3}{2} \text{O}_2(g) = 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l), \quad \Delta H_{298}^0 = -372.82 \text{ kcal}. \quad (5-20)
\]

Then \( \Delta H_{298}^0 \) for Eq. (5-17) must be \((-337.23) + (-68.32) - (-373.82) = -32.73 \text{ kcal} \). Notice that the result is not exactly the same as the directly determined value of \(-32.747 \text{ kcal} \). As mentioned earlier, the problem is that in using enthalpies of combustion we are combining very large numbers to give a small net result. Even small percentage errors in the former propagate to give a large percentage error in the result.
The example may be generalized. We may obtain $\Delta H_{298}^0$ for any reaction by adding the standard enthalpies of combustion of the reactants and subtracting the sum of those of the products:

$$\Delta H_{298}^0 = \sum_{\text{reactants}} n_r \Delta H_{c,298}^0 - \sum_{\text{products}} n_p \Delta H_{c,298}^0,$$  \hspace{1cm} (5-21)

where $\Delta H_{c,298}^0$ denotes a standard enthalpy of combustion. As an illustration, $\Delta H_{298}^0$ for the (unlikely) reaction

$$2 \text{CH}_4(g) + \text{CH}_3\text{COOH}(l) = \text{C}_3\text{H}_8(g) + \text{CO}_2(g) + 2 \text{H}_2(g)$$

is given by

$$2 \Delta H_{c,298}^0 (\text{CH}_4) + \Delta H_{c,298}^0 (\text{CH}_3\text{COOH}) - \Delta H_{c,298}^0 (\text{C}_3\text{H}_8) - 2 \Delta H_{c,298}^0 (\text{H}_2).$$

There is no term for $\text{CO}_2$ since by definition its enthalpy of combustion is zero. A table of standard enthalpies of combustion thus implies a knowledge of $\Delta H_{298}^0$ values for all reactions that can be formulated as a combination of combustion reactions.

5-5 Enthalpies of Formation

A. Standard Enthalpy of Formation for Compounds

A particularly useful way of summarizing thermochemical data is in terms of the standard enthalpy of formation. The reaction is that of formation of the compound from the elements, each element being in its stable chemical state and phase at 25°C and 1 atm pressure. For example, the reaction giving the standard enthalpy of formation of $\text{H}_2\text{O}(l)$, $\Delta H_{298}^0 (\text{H}_2\text{O}, l)$, is

$$\text{H}_2(g, 298 \text{ K}, 1 \text{ atm}) + \frac{1}{2} \text{O}_2(g, 298 \text{ K}, 1 \text{ atm}) = \text{H}_2\text{O}(l, 298 \text{ K}, 1 \text{ atm}).$$

(This particular enthalpy change is also that of the combustion of hydrogen.) That for methane is

$$\text{C(graphite, 298 K, 1 atm)} + 2 \text{H}_2(g, 298 \text{ K}, 1 \text{ atm}) = \text{CH}_4(g, 298 \text{ K}, 1 \text{ atm}),$$  \hspace{1cm} (5-22)

The heat of formation of an element in its standard state is zero by definition.

It is not always possible to determine a heat of formation directly, as in the case of water, and the values are usually calculated by the indirect procedure. Thus $\Delta H_{298}^0 (\text{CH}_4)$ could be obtained by application of Eq. (5-21) to the heats of combustion of graphite, hydrogen, and methane. Extensive tables of standard enthalpies of formation have been built up, and a sampling is given in Table 5-2. The table includes values for unstable forms of some elements, such as $\text{O}_3$, and $\text{C}$ (diamond) and in some cases also gives values for both gaseous and liquid states, as for water. The difference between two such values is simply the enthalpy of vaporization.

One may calculate the standard enthalpy change for any chemical reaction involving substances whose standard enthalpies of formation are known. The
<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta H^0_{f,298}$ kcal mole$^{-1}$</th>
<th>$\Delta H^0_{f,298}$ kJ mole$^{-1}$</th>
<th>Substance</th>
<th>$\Delta H^0_{f,298}$ kcal mole$^{-1}$</th>
<th>$\Delta H^0_{f,298}$ kJ mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl(s)</td>
<td>-30.36</td>
<td>-127.03</td>
<td>H$_2$O(l)</td>
<td>-68.317</td>
<td>-285.84</td>
</tr>
<tr>
<td>Br$_2$(g)</td>
<td>7.34</td>
<td>30.71</td>
<td>H$_2$O(g)</td>
<td>-57.789</td>
<td>-241.79</td>
</tr>
<tr>
<td>C(graphite)</td>
<td>(0.000)</td>
<td>(0.000)</td>
<td>HCl(g)</td>
<td>-22.063</td>
<td>-92.31</td>
</tr>
<tr>
<td>C(diamond)</td>
<td>0.4532</td>
<td>1.896</td>
<td>HBr(g)</td>
<td>-8.66</td>
<td>-36.23</td>
</tr>
<tr>
<td>CaCO$_3$(s)</td>
<td>-228.45</td>
<td>-1206.87</td>
<td>HI(g)</td>
<td>6.20</td>
<td>25.94</td>
</tr>
<tr>
<td>CaO(s)</td>
<td>-151.9</td>
<td>-635.5</td>
<td>KC1(s)</td>
<td>-104.175</td>
<td>-435.87</td>
</tr>
<tr>
<td>CO(g)</td>
<td>-26.416</td>
<td>-110.52</td>
<td>NaCl(s)</td>
<td>-98.232</td>
<td>-411.03</td>
</tr>
<tr>
<td>CO$_2$(g)</td>
<td>-94.052</td>
<td>-393.51</td>
<td>NH$_4$(g)</td>
<td>-11.04</td>
<td>-46.19</td>
</tr>
<tr>
<td>CH$_4$(g)</td>
<td>-17.89</td>
<td>-74.85</td>
<td>NO(g)</td>
<td>21.600</td>
<td>90.37</td>
</tr>
<tr>
<td>C$_2$H$_2$(g)</td>
<td>54.19</td>
<td>226.73</td>
<td>NO$_2$(g)</td>
<td>8.091</td>
<td>33.85</td>
</tr>
<tr>
<td>C$_2$H$_5$(g)</td>
<td>-20.24</td>
<td>-84.68</td>
<td>N$_2$O(g)</td>
<td>5.58</td>
<td>10.8</td>
</tr>
<tr>
<td>C$_2$H$_6$(g)</td>
<td>-24.82</td>
<td>-103.85</td>
<td>P(g)</td>
<td>75.18</td>
<td>314.6</td>
</tr>
<tr>
<td>C$_2$H$_6$(l)</td>
<td>11.718</td>
<td>49.028</td>
<td>PCl$_3$(g)</td>
<td>-95.35</td>
<td>-398.94</td>
</tr>
<tr>
<td>C$_2$H$_4$(g)</td>
<td>19.820</td>
<td>82.93</td>
<td>S(rhombic)</td>
<td>(0.000)</td>
<td>(0.000)</td>
</tr>
<tr>
<td>C$_2$H$_4$(l)</td>
<td>-66.356</td>
<td>-277.63</td>
<td>S(monoclinic)</td>
<td>0.071</td>
<td>0.30</td>
</tr>
<tr>
<td>CH$_3$COOH(l)</td>
<td>-116.4</td>
<td>-487.0</td>
<td>SO$_2$(g)</td>
<td>-70.96</td>
<td>-296.9</td>
</tr>
<tr>
<td>CCl$_4$(l)</td>
<td>-33.3</td>
<td>-139.3</td>
<td>SO$_3$(g)</td>
<td>-94.45</td>
<td>-395.2</td>
</tr>
<tr>
<td>Fe$_3$O$_4$(s)</td>
<td>-196.5</td>
<td>-822.2</td>
<td>Glycine</td>
<td>-126.33</td>
<td>-528.56</td>
</tr>
</tbody>
</table>


The combining rule is similar to Eq. (5-21) for heats of combustion, but reversed in sign (why?):

$$
\Delta H^0_{298} = \sum_{\text{products}} n_p \Delta H^0_{f,298} - \sum_{\text{reactants}} n_r \Delta H^0_{f,298}.
$$

As an example, we may calculate the heat of hydrogenation of ethylene [Eq. (5-17)] using heats of formation:

$$
\Delta H^0_{298} = \Delta H^0_{f,298} (C_2H_6(g)) - \Delta H^0_{f,298} (C_2H_4(g)) = -20.24 - 12.50 = -32.74 \ \text{kcal mole}^{-1}.
$$

There is no term for hydrogen because its heat of formation is zero by definition.

B. Standard Enthalpies of Aqueous Solutes and of Ions

Some values of enthalpies of solution were included in Table 5-1. Such data may be incorporated into the standard enthalpy of formation scheme by assigning the entire heat of solution to the solute. For example, the heat of dissolving of HCl (g) in water to give an infinitely dilute solution is, per mole of HCl, $-17.96$ kcal (Table 5-1). We use the notation $aq$ to denote the condition of infinite dilution, and may now write

$$
\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) = HCl(g), \quad \Delta H^0_{f,298} = -22.06 \ \text{kcal},
$$

$$
HCl(g) + aq = HCl(aq), \quad \Delta H^0_{298} = -17.96 \ \text{kcal}.
$$
Then we have

\[ \frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{Cl}_2(g) + aq = \text{HCl}(aq), \quad \Delta H^0_{f,298}(\text{HCl}, aq) = -40.02 \text{ kcal}. \]

The same convention may be applied to solutions of any concentration. Thus the standard enthalpy for the following reaction is $-17.65 \text{ kcal}$:

\[ \text{HCl}(g) + 100 \text{H}_2\text{O} = \text{solution of concentration } m = 0.55 \text{ mole per } 1000 \text{ g } \text{H}_2\text{O}, \quad \Delta H^0_{f,298} = -17.65 \text{ kcal}. \]

The standard enthalpy of formation of HCl in 0.55 molal solution is then $(-17.65) + (-22.06) = -39.71 \text{ kcal mole}^{-1}$.

In the case of infinitely dilute solutions of electrolytes it is convenient to proceed a step further. For such solutions the ions have no mutual interaction and the state of any given ion is entirely independent of the nature of its counter ion. It is therefore possible to combine equations as in the following example:

1. \( \frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{Cl}_2(g) = \text{H}^+(aq) + \text{Cl}^-(aq), \quad \Delta H^0_{f,298} = -40.02 \text{ kcal}, \)
2. \( \text{Na}(s) + \frac{1}{2} \text{Cl}_2(g) = \text{Na}^+(aq) + \text{Cl}^-(aq), \quad \Delta H^0_{f,298} = -97.30 \text{ kcal}, \)
3. \( \text{Na}(s) + \frac{1}{2} \text{Br}_2(l) = \text{Na}^+(aq) + \text{Br}^-(aq), \quad \Delta H^0_{f,298} = -86.18 \text{ kcal}, \)
4. \( = (a) + (c) - (b): \quad \frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{Br}_2(l) = \text{H}^+(aq) + \text{Br}^-(aq), \quad \Delta H^0_{f,298} = -28.90 \text{ kcal}. \)

HCl(aq) has been written as \( \text{H}^+(aq) + \text{Cl}^-(aq) \), and similarly for NaCl(aq) and NaBr(aq) not only because it is more nearly correct but also because it emphasizes that the \( \text{Cl}^-(aq) \) of the HCl solution cancels the \( \text{Cl}^-(aq) \) of the NaCl solution.

This procedure is unnecessarily clumsy. If the enthalpy of formation of some one ion were known, it would then be possible to calculate those of all other ions. Such a value is not known, since ionic chemical reactions always involve combinations of ions such that the equation is balanced electrically (see Section 13-CN-3 for a further comment). By the same token, however, one may arbitrarily assign a value to the standard enthalpy of formation of some one ion, and the values then calculated for the other ions must always occur in any thermochemical equation in such a way that the assumption cancels out. The convention is that \( \Delta H^0_{f,298}(\text{H}^+, aq) \) is zero.

Some representative standard enthalpies of formation of solutes and of individual aqueous ions are given in Table 5-3. We may now obtain the values of \( \Delta H^0_{f,298} \) for reactions (a), (b), (c), and (d) simply by adding the appropriate individual ion values.

### 5-6 Dependence of ΔH and ΔE on Temperature

The temperature dependence of individual \( H \) and \( E \) values is given by the equations

\[ dE = C_V \, dT \quad \text{[Eq. (4-22)]}, \]
\[ dH = C_p \, dT \quad \text{[Eq. (4-30)]}, \]
or, in integral form,

\[ E_2 = E_1 + \int_{T_1}^{T_2} C_v \, dT, \quad (5-24) \]

\[ H_2 = H_1 + \int_{T_1}^{T_2} C_p \, dT. \quad (5-25) \]

As discussed in Section 4-7C, heat capacities are in general temperature-dependent and the experimental values are usually summarized in the form of a polynomial in temperature. Three terms suffice to represent data over a considerable range of temperature. Thus we write\(^\dagger\)

\[ C_p = a + bT + cT^{-2}. \quad (5-26) \]

The polynomial formulation is convenient in allowing easy integration of Eq. (5-25). Values of \(a\), \(b\), and \(c\) are given in Table 5-4 for a number of gases, liquids, and solids.

The procedure for calculating the change in a heat of reaction with temperature is quite analogous to the preceding. Let \(\Delta H_2\) be the enthalpy of reaction at \(T_2\) and \(\Delta H_1\) that at \(T_1\). The general reaction equation (5-2) may then be written

\[ -\Delta H_2 = [aH_2(A) + bH_2(B) + \cdots] - [mH_2(M) + nH_2(N) + \cdots] \]

\[ = \left[a\left[H_1(A) + \int C_p(A) \, dT\right] + b\left[H_1(B) + \int C_p(B) \, dT\right] + \cdots\right] \]

\[ - \left[m\left[H_1(M) + \int C_p(M) \, dT\right] + n\left[H_1(N) + \int C_p(N) \, dT\right] + \cdots\right]. \]

\(^\dagger\) A widely used alternative power series is of the form \(C_p = a + bT + cT^2\).
TABLE 5-4. Variation of $C_p^0$ with Temperature\(^a\) $C_p^0 = a + bT + cT^{-2}$

<table>
<thead>
<tr>
<th>Substance</th>
<th>$a$</th>
<th>$10^b$</th>
<th>$10^{-c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gases (from 298 K to 2000 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monatomic gases</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>6.52</td>
<td>0.78</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>(27.28)</td>
<td>(3.26)</td>
<td>(0.50)</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>7.16</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(29.96)</td>
<td>(4.18)</td>
<td>(−1.67)</td>
</tr>
<tr>
<td>$\text{N}_2$</td>
<td>6.83</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(28.58)</td>
<td>(3.77)</td>
<td>(−0.50)</td>
</tr>
<tr>
<td>$\text{CO}$</td>
<td>6.79</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(28.41)</td>
<td>(4.10)</td>
<td>(−0.46)</td>
</tr>
<tr>
<td>$\text{Cl}_2$</td>
<td>8.85</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(37.03)</td>
<td>(0.67)</td>
<td>(−2.85)</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>10.57</td>
<td>2.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(44.23)</td>
<td>(8.79)</td>
<td>(−8.62)</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>7.30</td>
<td>2.46</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(30.54)</td>
<td>(10.29)</td>
<td></td>
</tr>
<tr>
<td>$\text{NH}_3$</td>
<td>7.11</td>
<td>6.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(29.75)</td>
<td>(25.10)</td>
<td>(−1.55)</td>
</tr>
<tr>
<td>$\text{CH}_4$</td>
<td>5.65</td>
<td>11.44</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(23.64)</td>
<td>(47.86)</td>
<td>(−1.92)</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_6$</td>
<td>2.46</td>
<td>60.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(10.29)</td>
<td>(251.9)</td>
<td></td>
</tr>
<tr>
<td>Liquids (from melting point to boiling point)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>18.04</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(75.48)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{I}_2$</td>
<td>19.20</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(80.33)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{NaCl}$</td>
<td>16.0</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(66.9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_6$</td>
<td>8.00</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(33.50)</td>
<td>(335)</td>
<td></td>
</tr>
<tr>
<td>Solids (from 298 K to melting point or 2000 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}$ (graphite)</td>
<td>4.03</td>
<td>1.14</td>
<td>−2.04</td>
</tr>
<tr>
<td></td>
<td>(16.86)</td>
<td>(4.77)</td>
<td>(−8.54)</td>
</tr>
<tr>
<td>$\text{Al}$</td>
<td>4.94</td>
<td>2.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(20.67)</td>
<td>(12.38)</td>
<td></td>
</tr>
<tr>
<td>$\text{Cu}$</td>
<td>5.41</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(22.64)</td>
<td>(6.28)</td>
<td></td>
</tr>
<tr>
<td>$\text{Pb}$</td>
<td>5.29</td>
<td>2.80</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>(22.13)</td>
<td>(11.72)</td>
<td>(0.96)</td>
</tr>
<tr>
<td>$\text{I}_2$</td>
<td>9.59</td>
<td>11.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(40.12)</td>
<td>(49.79)</td>
<td></td>
</tr>
<tr>
<td>$\text{NaCl}$</td>
<td>10.98</td>
<td>3.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(45.94)</td>
<td>(16.32)</td>
<td></td>
</tr>
</tbody>
</table>

On collecting terms, we obtain

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_P \, dT,$$

(5-27)

where the operator $\Delta$ in $\Delta C_P$ has its usual meaning. The coefficients $a$, $b$, and $c$ in the series expression for each individual heat capacity may be combined according to Eq. (5-27) so that $\Delta C_P$ may be written

$$\Delta C_P = \Delta a + (\Delta b)T + (\Delta c)T^{-2}.$$

(5-28)

A formal integration of Eq. (5-27) gives

$$\Delta H_2 = \Delta H_1 + (\Delta a)(T_2 - T_1) + \left(\frac{\Delta b}{2}\right)(T_2^2 - T_1^2) - (\Delta c)\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

(5-29)

The procedure is most commonly applied to $\Delta H^0$ values, that is, to $\Delta H$ quantities for 1 atm pressure, and the $C_P$ values of Table 5-4 are for this standard pressure. Analogous equations involving $C_V$ apply to the calculation of a $\Delta E_2$ from a $\Delta E_1$.

**Example.** Consider the reaction

$$\text{CH}_4(g) + 2\text{O}_2(g) = \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$$

We find $\Delta H^\circ_{298}$ from Table 5-2: $\Delta H^\circ_{298} = 2(-241.79) - 393.51 - (-74.85) = -802.24 \text{ kJ}.$

We obtain $\Delta H^\circ_{298}$ as follows, using Eq. (5-29): $\Delta a = 44.23 + 2(30.54) - 23.64 - 2(29.96) = 21.75 \text{ J K}^{-1}; \Delta b = [8.79 + 2(10.29) - 47.86 - 2(4.18)] \times 10^{-3} = -26.85 \times 10^{-3} \text{ J K}^{-2}; \Delta c = [-8.62 + 0 - (-1.92) - 2(-1.67)] \times 10^4 = -3.36 \times 10^4 \text{ J K}. \text{ Then}

$$\Delta H^\circ_{298} = -802.240 + 21.75(373.15 - 298.15)$$

$$\quad + \frac{-26.85 \times 10^{-3}}{2} [(373.15)^2 - (298.15)^2]$$

$$\quad - (-3.36 \times 10^4)\left(\frac{1}{373.15} - \frac{1}{298.15}\right)$$

$$\quad = -802.240 + 729 = -801.51 \text{ kJ}.$$

Equations (5-24) and (5-25) are applicable to a change of temperature which is not accompanied by any phase change. As illustrated in Fig. 5-2, a substance may exist in some phase $\alpha$ below a certain temperature and in some phase $\beta$ above that temperature. The most common situations are those in which $\alpha$ is a solid phase and $\beta$ the liquid phase, or in which $\alpha$ is the liquid phase and $\beta$ the gaseous one. If we take $H_1$ and $T_1$ as the reference points, then Eq. (5-25) is obeyed up to the temperature of the phase transition $T_{\alpha\beta}$. At this temperature additional heat is needed to bring about the transition and $H$ increases by the enthalpy of the transition $\Delta H_{\alpha\beta}$. Above $T_{\alpha\beta}$, $H$ again rises in accord with Eq. (5-25), although now the heat capacity is $C_P(\beta)$ rather than $C_P(\alpha)$. An entirely analogous analysis applies to the behavior of $E$.

The presence of phase transitions introduces a corresponding complication in the calculation of a $\Delta H_2$ from a $\Delta H_1$. In such a case Eq. (5-27) may still be used in the form

$$\Delta H_2 = \Delta H_1 + \sum_{\text{products}} n_p(H_2 - H_1) - \sum_{\text{reactants}} n_r(H_2 - H_1),$$

(5-30)
If a reactant or product undergoes a phase transition, this must be allowed for in calculating the corresponding \((H_2 - H_1)\) term; otherwise Eq. (5-25) is used in the usual manner.

**COMMENTARY AND NOTES**

### 5-CN-1 Explosions, Flames, and Rockets

The emphasis of this chapter has so far been on \(\Delta E\) and \(\Delta H\) quantities for reactions under standard conditions, and, in the preceding section, on the calculation of \(\Delta E\) or \(\Delta H\) at some temperature \(T_2\) given the value at \(T_1\). There is an interesting and important special case in which the chemical reaction occurs under essentially adiabatic conditions so that the heat of the reaction is confined to the system and therefore heats it as the reaction proceeds. This situation occurs in an explosion which takes place in an isolated system such as is approximated by an open flame and in the combustion of rocket fuel.

The confined explosion is the simplest case for us to treat more quantitatively. We can do so in terms of a generalized combustion reaction of a hydrocarbon using a scheme similar to that of the example of the preceding section:

\[
\begin{align*}
C_nH_{2n+2}(g, T_{\text{max}}) + \frac{3n+1}{2}O_2(g, T_{\text{max}}) & \rightarrow nCO_2(g, T_{\text{max}}) + (n + 1)H_2O(g, T_{\text{max}}) \\
C_nH_{2n+2}(g, 298 \text{ K}) + \frac{3n+1}{2}O_2(g, 298 \text{ K}) & \rightarrow nCO_2(g, 298 \text{ K}) + (n + 1)H_2O(g, 298 \text{ K})
\end{align*}
\]

\[\Delta E = q_1 = 0 \quad q_2 \quad (5-31)\]
To simplify matters, we avoid phase changes by specifying all species to be gaseous. Also, since the system is to be at constant volume, we must deal with $E$'s and $C_V$'s. We are interested in the value of $T_{\text{max}}$, the maximum temperature attained under adiabatic conditions. This means that the overall process is the one indicated by the arrow labeled $\Delta E = q_v = 0$. The desired $T_{\text{max}}$ may be calculated as follows.

We allow the reaction to proceed at 298 K and apply the heat of reaction to warming the products, which means the $q_v$ must just equal $\Delta E_{298}$:

$$0 = \Delta E_{298} + \int_{298K}^{T_{\text{max}}} [nC_v(CO_2) + (n + 1)C_v(H_2O)] dT$$

or, in general,

$$0 = \Delta E_{T_1} + \int_{T_1}^{T_{\text{max}}} \sum_{\text{products}} n_p C_v \, dT. \quad (5-32)$$

The heat capacities should be known as a function of temperature, and on carrying out the integration, one obtains an equation which is then to be solved for $T_{\text{max}}$.

**Example.** Referring to the preceding example, $\Delta H_{298}^0$ for the combustion of methane is $-804.24$ kJ. The temperature reached in an explosion is given by applying $\Delta E_{298}$ (also $-804.24$ kJ in this case) to heating the products. Assuming for simplicity that $C_v$ is $6R$ for both CO$_2$ and H$_2$O, the total $C_v$ is $(3)(6)(8.314) = 150 \text{ J K}^{-1}$ and $\Delta T = 804.240/150 = 5360$ K, or $T_{\text{max}} = 5660$ K.

Fundamental hazards to calculations of this type are the following. Since $\Delta E$ is negative, we expect from Le Châtelier's principle that the equilibrium will shift progressively to the left with increasing temperature. This means that combustion reactions which go to completion at 25°C may fail to do so at some very high temperature. An even more serious difficulty is that other equilibria begin to be important at very high temperatures. Water may be partly dissociated into H, HO, and O radicals; carbon dioxide begins to dissociate into CO and O$_2$ and further into C and O. Gases inert at room temperature, such as nitrogen, begin to enter into the reaction, and so on. All of these effects act either to reduce the amount of reaction or to expend some of the heat of the reaction in dissociating the products into fragments. The result is to reduce $T_{\text{max}}$ below its simple theoretical value, and often considerably so.

The problem becomes a very acute one in the field of aerospace engineering. A rocket exhaust is essentially a flame which has reached some high temperature by virtue of the heat of reaction of the propellants, and it is essential to know both the actual $T_{\text{max}}$ and the chemical composition of the exhaust if the thrust of the rocket is to be computed. The various dissociative equilibria mentioned here themselves depend on temperature, and the temperature reached depends on the extent of such dissociation. The consequence is that one must make a very involved series of successive approximations in order to arrive at a result.

### 5-CN-2 The Thermochemistry of Nutrition

The methods of thermochemistry have been applied extensively both to foods and to living systems. The overall processes that occur when food is metabolized
may be summarized as follows. For sugars and starches,

$$(\text{CH}_2\text{O})_n + n\text{O}_2 = n\text{CO}_2 + n\text{H}_2\text{O}(l), \quad \Delta H^\circ_{\text{comb}} \simeq 4 \text{ kcal g}^{-1}.$$  

Animal fats are likewise converted to $\text{CO}_2$ and $\text{H}_2\text{O}$. Taking tripalmitin as a typical example,

$$2\text{C}_{51}\text{H}_{98}\text{O}_6 + 145\text{O}_2 = 102\text{CO}_2 + 98\text{H}_2\text{O}(l), \quad \Delta H^\circ_{\text{comb}} \simeq 10 \text{ kcal g}^{-1}.$$  

In the case of proteins, the nitrogen appears in waste products, mainly urea. The combustion reaction is difficult to formulate precisely, but we can write in the case of glycine

$$2\text{H}_2\text{NCH}_2\text{COOH} + 3\text{O}_2 = \text{CO(NH}_2\text{)}_2(\text{aq}) + 3\text{CO}_2 + 3\text{H}_2\text{O}(l), \quad \Delta H^\circ_{\text{comb}} \simeq 2 \text{ kcal g}^{-1}.$$  

For an average protein $\Delta H^\circ_{\text{comb}}$ is usually taken to be 4.4 kcal g$^{-1}$. In obtaining the "calorie" content of a food (in nutrition the word "calorie" actually means kilocalorie) it is first fractionated into the sugar + starch, fat, and protein components. One then applies the foregoing heats of combustion to obtain an overall calorie rating for the food.

The equations above do give the approximate net change that occurs in metabolism. One way of checking this conclusion is to measure the respiratory quotient, R.Q., which is the ratio of moles of $\text{CO}_2$ produced to moles of $\text{O}_2$ consumed by the subject. R.Q. should be about 1 for sugars and starches, about 0.7 for fats, and about 0.8 for proteins. In the case of a group of human subjects, the observed average R.Q. rose toward unity on a carbohydrate diet, and fell toward 0.7 on a fat diet.

In another approach, actual calorimetry is done on test subjects, to determine the rate of metabolic evolution of heat. The total oxidation occurring is calculated from the amount of $\text{CO}_2$ exhaled, supplemented by analyses of the excreta. The calculated heat production can then be compared with that from the whole body calorimetry. As an example, direct calorimetry on a group of men gave 2250 kcal as the heat produced in a 24-hour day under resting conditions, and 4690 kcal under working conditions. The calculated values were 2450 kcal and 4700 kcal, respectively. Thus most of the calorie content of a person's diet is accounted for chemically [see Gemmill and Brobeck (1968)]. Note Fig. 5-3 for an interesting space-age application.

The finding that most of the energy content of food appears as work and heat is a reflection of the fact that the adult organism is not growing. Growth adds to the physical size, and the nutrients that go into new tissue cannot, of course, appear as combustion products. The adult uses food energy to do physical work and to keep the body in its nonequilibrium steady state. Examples of this last category include the energy needed for the regeneration of cells, to supply the heat dissipated by friction within the body, as in blood circulation, and to maintain body temperature.
bond energy is simple in the case of a diatomic molecule; it is just the dissociation energy. Thus

\[ \text{H}_2(g) = 2\text{H}(g), \quad \Delta H_{298}^0 = 104.2 \text{ kcal}, \tag{5-33} \]

\[ \text{HI}(g) = \text{H}(g) + I(g), \quad \Delta H_{298}^0 = 71.4 \text{ kcal}. \tag{5-34} \]

The H—H and H—I bond energies are then 104.2 and 71.4 kcal, respectively.
An alternative to the foregoing is to use $\Delta E_0$ values for bond energies where, as indicated in Fig. 4-11, $\Delta E_0$ is the energy to take a diatomic molecule from the lowest or zero-point vibrational state to the dissociation limit. Spectroscopy gives $\Delta E_0$ values. There is undoubtedly some confusion in that spectroscopic $\Delta E_0$ values and thermochemical $\Delta H^\circ_{298}$ values have been used somewhat interchangeably. The two values are not greatly different, however. For example, $\Delta E_0$ for the atomization of hydrogen is 103.2 kcal, as compared to the $\Delta H^\circ_{298}$ of 104.2 kcal. The practice here will be to use the standard enthalpies.

Bond energies may also be obtained for polyatomic molecules. The enthalpy of atomization of methane is taken to be four times the average C—H bond energy:

$$\text{CH}_4(g) = \text{C}(g) + 4\text{H}(g), \quad \Delta H^\circ_{298} = 397.2 \text{ kcal.} \quad (5-35)$$

The average C—H bond energy is then 99.3 kcal. The $\Delta H^\circ_{298}$ value is obtained by summing the following steps:

$$\begin{align*}
\text{CH}_4(g) &= \text{C(graphite)} + 2\text{H}_2(g), \quad \Delta H^\circ_{298} = 17.9 \text{ kcal,} \\
2\text{H}_2(g) &= 4\text{H}(g), \quad \Delta H^\circ_{298} = 208.4 \text{ kcal,} \\
\text{C(graphite)} &= \text{C}(g), \quad \Delta H^\circ_{298} = 170.9 \text{ kcal,} \\
\text{CH}_4(g) &= \text{C}(g) + 4\text{H}(g), \quad \Delta H^\circ_{298} = 397.2 \text{ kcal.}
\end{align*}$$

(5-36)

Among these values the heat of sublimation of graphite has been the most uncertain because of the great experimental difficulties involved; as a result, several values appear in the chemical literature. For this reason, different references may report somewhat different C—H bond energies. It should also be stressed that the value given here is the average C—H bond energy. The process of dissociating one hydrogen atom at a time to give CH$_3$, CH$_2$, CH, and then C will require somewhat different energies for each step; that for the first step is estimated to be 102 kcal, for example. The H—O bond energy may be obtained from the sum of reactions

$$\begin{align*}
\text{H}_2\text{O}(g) &= \text{H}_2(g) + \frac{1}{2}\text{O}_2(g), \quad \Delta H^\circ_{298} = 57.8 \text{ kcal,} \\
\text{H}_2(g) &= 2\text{H}(g), \quad \Delta H^\circ_{298} = 104.2 \text{ kcal,} \\
\frac{1}{2}\text{O}_2(g) &= \text{O}(g), \quad \Delta H^\circ_{298} = 59.2 \text{ kcal,} \\
\text{H}_2\text{O}(g) &= 2\text{H}(g) + \text{O}(g), \quad \Delta H^\circ_{298} = 221.2 \text{ kcal.}
\end{align*}$$

(5-37)

There are two H—O bonds in water, and so the average H—O bond energy is 111 kcal. The N—H bond energy follows from an analogous calculation involving ammonia.

We next assume that bond energies are additive, that is, that the strength of a given type of bond is independent of its chemical environment. For example, the enthalpy of dissociation of ethane into atoms can be calculated from its enthalpy of formation and the enthalpies of sublimation of graphite and of dissociation of hydrogen. We get

$$\text{C}_2\text{H}_6(g) = 2\text{C}(g) + 6\text{H}(g), \quad \Delta H^\circ_{298} = 674.6 \text{ kcal.}$$

Ethane consists of six C—H bonds and one C—C bond, and the assumption is
that the sum of these bond dissociation energies should equal the overall enthalpy of atomization. The C—H bond is taken to be the same as the average value in methane, so that the C—C bond energy should be 674.6 — 595.8 = 78.8 kcal. Repetition of the same type of calculation for propane leads to a C—C bond energy of 78 kcal, so the assumption is at least approximately correct. Application of the above procedure to methanol yields a C—O bond energy, and so on.

A number of such bond strengths are given in Table 5-5 along with some useful heats of sublimation of elements. Note that the value given there for the C—C and C—H bond energies are somewhat different than the ones just obtained. The figures in the table are offered as better average values for general use.

In some cases the discrepancy between an observed enthalpy and that calculated from bond energies appears to be real—that is, due to a specific, neglected factor. For example, one obtains from the enthalpies of formation of benzene and of atomization of graphite and hydrogen

\[ \Delta H^0_{298} = 1318 \text{ kcal}. \]  

\[ C_6H_6(g) = 6C(g) + 6H(g), \]

Benzene, if written in the Kekulé structure

\[
\begin{array}{c}
\text{H} \\
\text{H—C—C—C—C—H} \\
\text{H—C—C—C—H} \\
\text{H} \\
\end{array}
\]

would be assigned six C—H bonds, three C—C bonds, and three C=C bonds, which total 1284 kcal. The discrepancy of 34 kcal suggests that benzene is more stable than expected in terms of this structure. The modern explanation is that there are no fixed C=C bonds and that the electrons which might go into such bonds interact instead in a diffuse or delocalized way and are spread over the whole molecule. This difference between the estimated energy of a fixed bond structure and the actual energy of a delocalized bonding structure is called the resonance energy.

Although the assumption of additivity of bond strengths can lead to appreciable error, it does provide a means of estimating enthalpies of formation of compounds not yet studied or difficult to study. In the case of flames, for example, one may need an estimate of the enthalpies of formation of various radicals. A similar situation occurs in chemical kinetics, where it is desirable to estimate the energy required to produce possible reaction intermediates [see Benson (1968)].

5-ST-2 Internal Energy and Enthalpy Functions

The fact that we do not know absolute values for internal energies and enthalpies is reflected in our procedures in thermochemistry. Thus we tabulate standard
TABLE 5-5. **Enthalpies of Formation of Atoms and Bond Strengths**

<table>
<thead>
<tr>
<th>Atom</th>
<th>$\Delta H^0_{298}$</th>
<th>Bond</th>
<th>$\Delta H^0_{298}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kcal mole$^{-1}$</td>
<td>kJ mole$^{-1}$</td>
<td>kcal mole$^{-1}$</td>
</tr>
<tr>
<td>H</td>
<td>52.1</td>
<td>218.0</td>
<td>C–H</td>
</tr>
<tr>
<td>O</td>
<td>59.2</td>
<td>247.7</td>
<td>C–C</td>
</tr>
<tr>
<td>N</td>
<td>112.9</td>
<td>472.4</td>
<td>C=O</td>
</tr>
<tr>
<td>S</td>
<td>53.2</td>
<td>223.8</td>
<td>C–O</td>
</tr>
<tr>
<td>P</td>
<td>75.2</td>
<td>314.6</td>
<td>C–O</td>
</tr>
<tr>
<td>C</td>
<td>170.9</td>
<td>715.0</td>
<td>C–N</td>
</tr>
<tr>
<td>F</td>
<td>18.3</td>
<td>76.6</td>
<td>C–O</td>
</tr>
<tr>
<td>Cl</td>
<td>29.0</td>
<td>121.3</td>
<td>C–O</td>
</tr>
<tr>
<td>Br</td>
<td>26.7</td>
<td>111.7</td>
<td>C–O</td>
</tr>
<tr>
<td>I</td>
<td>25.5</td>
<td>106.7</td>
<td>O–H</td>
</tr>
<tr>
<td>Na</td>
<td>26.0</td>
<td>108.8</td>
<td>O–O</td>
</tr>
<tr>
<td>K</td>
<td>21.5</td>
<td>90.0</td>
<td>C–N</td>
</tr>
<tr>
<td>Ca</td>
<td>46.0</td>
<td>192.4</td>
<td>C–N</td>
</tr>
<tr>
<td>Al</td>
<td>75.0</td>
<td>313.8</td>
<td>Cl–Cl</td>
</tr>
<tr>
<td>Ni</td>
<td>102</td>
<td>426.8</td>
<td>Br–Br</td>
</tr>
<tr>
<td>Ag</td>
<td>69.1</td>
<td>289.1</td>
<td>I–I</td>
</tr>
</tbody>
</table>


** From their standard states.

Enthalpies of formation of substances and not their absolute enthalpies. That is, we take the elements in their standard state as a point of reference. Since we are interested in $\Delta H$ or $\Delta E$ for a chemical reaction, only the differences between enthalpies or energies of formation are involved, and the choice of reference state cancels out. Were the absolute $H$ and $E$ values known for the elements, we could then convert all of the standard heats of formation to absolute values. However, such a set of values would lead to exactly the same $\Delta H$ or $\Delta E$ for a chemical process as before. (The proof of this statement is left as an exercise.)

The choice of reference state is therefore mainly a matter of convenience. Although the usual choice is well suited for the compilation of thermochemical data, there is an alternative, a more natural one from the point of view of statistical thermodynamics. This alternative may be introduced as follows. By Eq. (4-22),

$$\left(\frac{\partial E}{\partial T}\right)_V = c_V,$$

where, it will be recalled, $E$ is the average energy per molecule. Integration then gives

$$E = E_0 + \int_0^T c_V dT. \quad (5-39)$$

The energy $E_0$ is the energy per molecule at 0 K and hence the energy in the lowest translational, rotational, vibrational, and electronic energy state. The first two we regard as zero, the third is the zero-point energy, $\frac{1}{2} \hbar v$, and the fourth is unknown. In fact, $E_{0,\text{elec}}$ is essentially unknowable, since our experience, as
embodied in the first law, is that we can only determine changes in energy and not absolute values. If we now define a quantity $E - E_0$, the internal energy function, we have

$$E - E_0 = \int_0^T c_v \, dT$$  \hspace{1cm} (5-40)

and the quantity on the right is in principle experimentally determinable. It is, for example, actually $E - E_0$ that is given by Eq. (4-55),

$$E - E_0 = kT^2 \left[ \frac{\partial (\ln Q)}{\partial T} \right]_V.$$  \hspace{1cm} (5-41)

or, per mole,

$$E - E_0 = RT^2 \left[ \frac{\partial (\ln Q)}{\partial T} \right]_V.$$  \hspace{1cm} (5-42)

The statistical thermodynamic treatment in Chapter 4 showed that it is usually possible to factor a partition function into the separate translational, rotational, and vibrational contributions. Thus

$$E - E_0 = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}}.$$  \hspace{1cm} (5-43)

Also, from the definition of $H$,

$$H - E_0 = (E - E_0) + PV$$  \hspace{1cm} (5-44)

and

$$H^0 - E_0 = (E - E_0) + PV,$$  \hspace{1cm} (5-45)

where the zero superscript denotes that $H$ is for the standard pressure of 1 atm; $H^0 - E_0$ is the standard enthalpy function. For an ideal gas,

$$H^0 - E_0 = (E - E_0) + RT \quad \text{(ideal gas)}.$$  \hspace{1cm} (5-46)

The standard enthalpy function may be related to experiment as follows. For the general reaction

$$aA + bB + \cdots = mM + nN + \cdots,$$

we can write $\Delta H^0$ for some temperature $T$ as

$$\Delta H^0_T = \Delta (H^0 - E_0)_T + \Delta E_0.$$  \hspace{1cm} (5-47)

If we know $\Delta (H^0 - E_0)_T$, $\Delta E_0$ can be calculated from the experimental heat of reaction. Since $\Delta E_0$ is the internal energy change when the reaction occurs with each species in its lowest energy state, it is a fundamental quantity for the reaction. Thus $\Delta H^0_T$ has been written as the sum of $\Delta E_0$, about which nothing can be calculated, and a term $\Delta (H^0 - E_0)_T$, which can be calculated. It is a way of concentrating the full capabilities of thermodynamics into a single term.

We can now proceed to examine the calculation of $(H^0 - E_0)_T$ for a substance. There are two independent ways of doing this. First, we can obtain $(E - E_0)_T$

$^{\dagger}$ More often, this term is applied to $(H^0 - H^0_0)/T$ as discussed in Section 6-ST-3.
and hence \((H^0 - E_0)_T\) by means of Eq. (5-40). This requires a complete knowledge of the heat capacity of the substance from 0 K up to the desired temperature. If phase changes occur in the process of heating the substance from 0 K, then the energies of these changes must be included, essentially in the manner indicated in Fig. 5-2. Alternatively, \((H^0 - E_0)_T\) could be obtained from a similar heating at constant pressure and from the variation of \(C_P\) with temperature and the enthalpies of any phase changes. This approach is discussed further in Section 6-ST-3.

The heat capacity approach does not really add anything over the discussion in Section 5-6 on the temperature dependence of \(\Delta H\) and \(\Delta E\). It is of more importance that \((H^0 - E_0)_T\) can be calculated by the methods of statistical thermodynamics. Thus if the various energy states are known, \((H^0 - E_0)_T\) can be obtained directly through Eq. (5-43). By repeating the calculation for each substance involved in a chemical reaction, one then obtains \(\Delta(H^0 - E_0)_T\) and, by means of Eq. (5-47), \(\Delta E_0\). Having \(\Delta E_0\), one can now calculate \(\Delta H^0\) for any temperature. There are some considerable further advantages to the use of enthalpy functions in dealing with applications of the second law of thermodynamics; these are discussed in the Special Topics section of the next chapter.

**Example.** To illustrate the application of statistical thermodynamics to thermochemistry, consider the reaction

\[
3\text{H}_2 + \text{N}_2 = 2\text{NH}_3, \quad \Delta H^0_{298} = -22.08 \text{ kcal.} \tag{5-48}
\]

We assume that each gas is ideal and can apply the methods of Chapter 4 to the calculation of \(E - E_0\) for each species. It is safe to assume that at 25°C the equipartition values will be reached with respect to the translational and rotational contributions. The calculations then center on obtaining \(E_{\text{vib}}\); we use Eq. (4-81) and need the fundamental frequency or characteristic vibrational temperature \(\theta_{\text{vib}}\) for each mode of vibration. The latter is given by \(\theta_{\text{vib}} = \frac{h v_0}{k}\) or, if \(v_0\) is in cm\(^{-1}\), \(\theta_{\text{vib}} = \frac{hcv_0}{k} = 1.4399\). Then \(E_{\text{vib}}\) is [Eq. (4-82)]

\[
E_{\text{vib}} = RT \frac{x}{e^x - 1} = RTf(x),
\]

where \(x = \theta_{\text{vib}}/T\) and \(f(x) = x/(e^x - 1)\).

The calculation for each species may be assembled as follows.

**Hydrogen**
- translation: \(E_{\text{trans}} = \frac{3}{2}RT = 888\) cal
- rotation: \(E_{\text{rot}} = RT = 592\) cal
- vibration: \(v_0 = 4160.2 \text{ cm}^{-1}\), \(\theta_{\text{vib}} = 5987\) K, \(x = 20.08, f(x) = 0.0000:\)
  \(E_{\text{vib}} = RTf(x) = 0\) cal
- total: \(1480\) cal

**Nitrogen**
- translation: same as for \(\text{H}_2\)
- rotation: same as for \(\text{H}_2\)
- vibration: \(v_0 = 2230.7 \text{ cm}^{-1}\), \(\theta_{\text{vib}} = 3210\) K, \(x = 10.77, f(x) = 0.0003:\)
  \(E_{\text{vib}} = 0.0003RT = 0\) cal
- total: \(1480\) cal

**Ammonia**
- translation: same as for \(\text{H}_2\) and \(\text{N}_2\)
- rotation: \(E_{\text{vib}} = \frac{3}{2}RT = 888\) cal
vibration: there are six vibrational degrees of freedom, but only four frequencies since two are doubly degenerate; thus

\[ v_1 = 3337 \text{ cm}^{-1}, \text{ from which } f(x) = 0.0000; \]
\[ E_1 = 0 \text{ cal} \]
\[ v_2 = 950 \text{ cm}^{-1}, f(x) = 0.047; \]
\[ E_2 = 0.047RT = 28 \text{ cal} \]
\[ v_3 = 3414 \text{ cm}^{-1} \text{ (twice); } f(x) = 0.0000; \]
\[ E_3 = 0 \text{ cal} \]
\[ v_4 = 1627.5 \text{ cm}^{-1} \text{ (twice); } f(x) = 0.003; \]
\[ E_4 = (0.003)2RT = 4 \text{ cal} \]

The value of \( \Delta(E - E_0) \) is then

\[ \Delta(E - E_0) = 2(1808) - 1480 - 3(1480) = -2304 \text{ cal} \]

and

\[ \Delta(H^0 - E_0) = -2304 - 2RT = -3489 \text{ cal}. \]

Finally, from Eq. (5-47),

\[ \Delta E_0 = -22.08 - (-3.49) = -18.59 \text{ kcal.} \]

Knowing \( \Delta E_0 \), we could repeat the entire calculation for any other temperature to obtain a \( \Delta H^0 \) for that temperature. The temperature could, for example, be one not easily accessible for direct experimental measurements.

The preceding discussion illustrates several points. First we see again that the energy of an ideal gas is a function of temperature only; the calculations of \( E - E_0 \) did not require a value for the pressure. Second, the major contributions to \( E - E_0 \) were from translation and rotation. This will generally be true for small, strongly bonded molecules around 25°C (the discussion of Section 4-12 on the molecular interpretation of heat capacities is relevant at this point). Considerations such as this last one are often helpful in estimations of the vibrational contribution when quantitative information is not available. Thus the use of the enthalpy function allows an intermixing of phenomenological or classical thermodynamics and statistical thermodynamics.

GENERAL REFERENCES


CITED REFERENCES

5-1  Calculate $\Delta H_{298}^\circ$ and $\Delta E_{298}$ for the reaction

$$\text{C}_2\text{H}_4(g) + \text{CH}_3\text{COOH}(l) + \text{NH}_3(g) = 2\text{CH}_4(g) + \text{H}_2\text{NCH}_2\text{COOH}(s).$$

*Ans.* $\Delta H_{298}^\circ = -14.43 \text{ kcal or } -60.38 \text{ kJ}$; $\Delta n_e = 0$ so $\Delta E = \Delta H$.

5-2  Calculate $\Delta H_{298}^\circ$ and $\Delta E_{298}$ for the incomplete combustion reaction

$$\text{C}_2\text{H}_4(g) + \frac{1}{2} \text{O}_2(g) = 6\text{C}(s) + 3 \text{H}_2\text{O}(l).$$

*Ans.* $\Delta H_{298}^\circ = -224.77 \text{ kcal or } -940.4 \text{ kJ}$; $\Delta E = -223.29 \text{ kcal or } -934.2 \text{ kJ}$.

5-3  Calculate $\Delta H_{298}^\circ$ for the combustion of glycine.$^{29}$

*Ans.* $-232.57 \text{ kcal or } -973.1 \text{ kJ}$.

5-4  Calculate $\Delta H_{298}^\circ$ per mole for the *cis to trans* isomerization of $\text{CH}_3\text{CH}=\text{CHCH}_3$.

*Ans.* $-949 \text{ cal or } -3.97 \text{ kJ}$.

5-5  A small catalytic hydrogenation unit has a heat capacity of 300 cal K$^{-1}$. What will its rate of heating be if an equimolar mixture of ethylene and hydrogen gases is passed through it at the rate of 2 millimoles of mixture per minute? Assume complete reaction.

*Ans.* $0.109^\circ \text{C min}^{-1}$.

5-6  A sample consisting of 0.200 g of CH$_3$COOH($l$) is ignited in a bomb calorimeter containing pure oxygen. The heat capacity of the calorimeter is 12,000 J °C$^{-1}$. What temperature increase should occur?

*Ans.* $0.242^\circ \text{C}$.

5-7  Calculate $\Delta H_{298}^\circ$ for the process

$$\text{Ag} + \text{HCl}($aq$) = \text{AgCl}(s) + \frac{1}{2}\text{H}_2(g).$$

The heat of formation of AgCl(s) is $-127.0 \text{ kJ}$.

*Ans.* $40.5 \text{ kJ or } 9.67 \text{ kcal}$.

5-8  Obtain $\Delta H_{298}^\circ$ for the formation of NH$_4$OH($aq$).

*Ans.* $-86.70 \text{ kcal or } 363 \text{ kJ}$.

5-9  What is $\Delta H_{298}^\circ$ for the dilution process NaOH (in 100 moles H$_2$O) = NaOH($aq$)?

*Ans.* $-128 \text{ cal or } -536 \text{ J}$.

5-10 Calculate $\Delta H_{2}^\circ$ of NH$_3$ at 500$^\circ$C.

*Ans.* $-12.84 \text{ kcal or } -53.7 \text{ kJ}$.

5-11 Calculate $\Delta H_{2}^\circ$ of CH$_3$COOH($g$) at 100$^\circ$C given that $\Delta H_{v}$ is 405 J g$^{-1}$ at the normal boiling point or 118$^\circ$C and that the values of $C_P$ are 2.30 J °C$^{-1}$ g$^{-1}$ and 6.27 J °C$^{-1}$ g$^{-1}$ for liquid and gaseous acetic acid, respectively.

*Ans.* $-111.1 \text{ kcal mole}^{-1} \text{ or } -464.8 \text{ kJ mole}^{-1}$. 

Remember to take as exact numbers given to one significant figure. Give your answers in kilocalories and in kilojoules.
5-12 How many m$^3$ of water (liquid) would be obtained if 0.1 kg of C(graphite) were burned to CO$_2$ in an ice calorimeter?

*Ans.* $5.452 \times 10^{-4}$ m$^3$.

**PROBLEMS**

Problems marked with an asterisk require fairly lengthy computations.

5-1 Calculate $\Delta H^{\circ}_{298}$ and $\Delta E^{\circ}_{298}$ in kilocalories and in kilojoules for the reaction

$$C_2H_4(\text{g}) + H_2(\text{g}) + \frac{1}{2}O_2(\text{g}) = C_2H_5OH(\text{l}).$$

5-2 Calculate $\Delta H^{\circ}_{298}$ and $\Delta E^{\circ}_{298}$ in kilocalories and in kilojoules for the reaction

$$2H_2O(\text{l}) + CCl_4 + 3SO_2 = S(\text{monoclinic}) + CO_2 + 4HCl(\text{g}) + 2SO_3(\text{g}).$$

5-3 The heat of sublimation of graphite to carbon atoms has been estimated as 170 kcal mole$^{-1}$. The dissociation of molecular hydrogen into atoms, H$_2$ = 2H, has $\Delta H^0 = 103.2$ kcal mole$^{-1}$. From these data and the value for the heat of formation of methane, calculate $\Delta H^0$ for

$$C(g) + 4H(g) = CH_4(g).$$

One-fourth of this value is a measure of the C–H bond energy in methane.

5-4 At 25°C and constant pressure, the heat of formation of CO$_2$ from graphite is $-94.272$ kcal mole$^{-1}$ and the heat of combustion of CO is $-67.263$ kcal mole$^{-1}$. Calculate $\Delta H$ for the formation of one mole of CO from C and CO$_2$ (at 1000 K) if the following equations are valid for the molar heat capacities:

- for C (graphite): $C_p = 1.20 + 0.0050T - 1.2 \times 10^{-4}T^2$;
- for CO$_2(g)$: $C_p = 7.40 + 0.006T - 1.50 \times 10^{-6}T^2$;
- for CO(g) and O$_2(g)$: $C_p = 6.5 + 0.0010T$.

5-5 For the following reaction at 25°C, $\Delta H = -56$ kcal:

$$2HI(\text{g, 1 atm}) + Cl_2(\text{g, 1 atm}) = 2HCl(\text{g, 1 atm}) + I_2(\text{s}).$$

Given that the heat of sublimation of I$_2(s)$ is 6.1 kcal mole$^{-1}$ at 185°C; the heat capacities $C_p$ for the gases HI, HCl, Cl$_2$, and I$_2$ may be taken to be 6.5 cal °C$^{-1}$ mole$^{-1}$ and independent of temperature; the heat capacity $C_p$ for I$_2(s)$ is 12.6 cal °C$^{-1}$ mole$^{-1}$ (independent of T); calculate $\Delta H$ for the following reaction at 125°C:

$$2HI(\text{g, 1 atm}) + Cl_2(\text{g, 1 atm}) = 2HCl(\text{g, 1 atm}) + I_2(\text{g, 1 atm}).$$

5-6 Calculate the maximum temperature achieved by the mixture when 0.100 g of methane gas is exploded in a constant-volume adiabatic (that is, insulated) calorimeter containing 10 g of air. The initial temperature is 25°C. Assume ideal gas behavior.

5-7 One-half mole of methane at 25°C is exploded in a large excess, ten moles, of oxygen, burning completely to carbon dioxide and water. Calculate the final temperature under adiabatic conditions (a) assuming the explosion to be at constant pressure, (b) assuming it to be at constant volume.
5-8 Calculate (a) $\Delta H^\circ_{298}$ for the reaction $\frac{1}{2}H_2 + \frac{1}{2}N_2 + CH_4 + CO_2 = H_2NCH_2COOH(s)$ 
and (b) $\Delta H^\circ_{298}$ and $\Delta E_{298}$ for the combustion of $H_2NCH_2COOH(s)$ to $CO_2$ and $H_2O(l)$.

5-9 $\Delta H^\circ_{298}$ is 71.4 kcal for the reaction $HI(g) = H(g) + I(g)$. $C_P$ for HI is $5.00 + 1 \times 10^{-3}T$ in cal K$^{-1}$ mole$^{-1}$. The bond energy of HCl at 25°C is 103 kcal mole$^{-1}$. Calculate (a) $\Delta H^\circ$ and $\Delta E$ for the atomization of HI(g) at 1000 K, and (b) $\Delta H^\circ_{298}$ for HI + I = H + Cl.

5-10 The heats of combustion at 25°C and 1 atm of cyclopropane, [(CH$_2$)$_3$], graphite, and hydrogen are $-499.85$ kcal mole$^{-1}$, $-94.051$ kcal mole$^{-1}$, and $-68.317$ kcal mole$^{-1}$, respectively [values for graphite and hydrogen are from Wagman et al. (1945)]. At 25°C, $\Delta H$ for the formation of propene, CH$_3CH=CH_2$, from the elements is 4.879 kcal (Brosen and Rossini, 1946). Find $\Delta H$ for (a) the formation of one mole of cyclopropane from the elements, (b) the isomerization of one mole of cyclopropane at 25°C and 1 atm (Knowlton and Rossini, 1949).

5-11 Calculate $\Delta H^\circ_{298}$ for the process

$$HCl(aq) + NaOH(aq) = NaCl(aq) + H_2O.$$ Estimate the value for the same reaction if the solutions are about 0.5 molal.

5-12 The temperature of a hydrogen–oxygen flame is found to be 2000 K. Assuming constant-pressure conditions and that oxygen is initially present in a threefold molar excess over hydrogen (that is, 3:1 mole ratio), calculate the degree of combustion of the hydrogen to water.

5-13* Find a, b, and c values for the equation $C_P^0 = a + bT + cT^2$ that fit the data for CO$_2$ over the range 298 K to 2000 K. (Heat capacity data are often reported in this form.) Use Eq. (5-26) and Table 5-4 to generate your data. Using calculated points at 200 K intervals, find the a, b, and c values giving the best least squares fit.

5-14 Calculate $\Delta H^\circ$ at 90°C for the combustion of C$_6$H$_6(g)$ to CO$_2(g)$ and H$_2$O(g). Use only the following data. Substance ($C_P$ in J K$^{-1}$ mole$^{-1}$): C$_6$H$_6(l)$(130); C$_6$H$_6(g)$(100); O$_2(g)$(30); CO$_2(g)$(47); H$_2$O (l) (75); H$_2$O(g) (34). Also the enthalpies of vaporization are 34,000 and 44,000 J mole$^{-1}$ for C$_6$H$_6$ and for H$_2$O, respectively, at their normal boiling points of 80°C and 100°C. The standard enthalpy of combustion of C$_6$H$_6(l)$ to H$_2$O(l) is $-3268$ kJ mole$^{-1}$ at 25°C.

5-15 An aqueous solution of Cr(NH$_3$)$_3$$^+$ is totally absorbing to 450 nm light. Ten cm$^3$ of solution at 25°C is irradiated for 10 sec with an incident intensity of $8.00 \times 10^{14}$ quanta sec$^{-1}$ and a temperature rise of 0.00950°C is observed. Calculate $\Delta H$ for the reaction Cr(NH$_3$)$_3$$^+$ + H$_2$O = Cr(NH$_3$)$_3$(H$_2$O)$^{2+}$ + NH$_3$(aq) if this is the photochemical reaction and the quantum efficiency is 0.36 (that is, 0.36 mole of reaction occurs for every mole of light quanta absorbed). Assume the heat capacity of the solution is that for water.

SPECIAL TOPICS PROBLEMS

5-1 Calculate $\Delta H^\circ_{298}$ for formation of isobutene, using bond energies.

5-2 The standard heat of combustion of naphthalene (solid) is $-1231$ kcal mole$^{-1}$ at 25°C (to CO$_2$ and liquid water) and the heat of sublimation is about 9 kcal mole$^{-1}$. Estimate the resonance energy for naphthalene.
5-3 Calculate $E_0$ for the reaction $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) = \text{CO}_2(g)$ from the known $\Delta H^0$ at 25°C and the spectroscopic constants as given in Table 6-1. Then calculate $\Delta H^0$ for the reaction at 1000°C. Compare your result with the value obtained using the heat capacity expressions of Table 5-4 and the value of $\Delta H^0$ at 25°C. $B_0$ is 0.3906 cm$^{-1}$ for $\text{CO}_2$, a linear molecule, and the fundamental vibration frequencies are $v_1 = 1388.3$ cm$^{-1}$, $v_2 = 667.3$ cm$^{-1}$ (twice), and $v_3 = 2349.3$ cm$^{-1}$. Note Table 6-1.